



(51) International Patent Classification:

C11D 3/22 (2006.01) *C11D 17/00* (2006.01)
C11D 3/37 (2006.01)

(21) International Application Number:

PCT/US2014/061992

(22) International Filing Date:

23 October 2014 (23.10.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13190513.5 28 October 2013 (28.10.2013) EP

(71) Applicants: **DOW GLOBAL TECHNOLOGIES LLC**

[US/US]; 2040 Dow Center, Midland, MI 48674 (US).
ROHM AND HAAS COMPANY [US/US]; 100 Independence Mall West, Philadelphia, PA 19106 (US).

(72) Inventors: **OBERLIN, Anne**; 897 chemin des Ames du

Purgatoire, Résidence Anais, F-06600 Antibes (FR).

THEUERKAUF, Jorg; 203 Plum Circle, Lake Jackson,

TX 77566 (US). **NOVEMBER, Samuel**; 150 Hartford

Lane, Newtown, PA 18940 (US). **DEPOOT, Karel Jozef**

Maria; 1853 Strombeek-Bever, B-100 Tenselaan (BE).

(74) Agent: **SHALTOUT, Raef**; The Dow Chemical Company,

Intellectual Property, P.O. Box 1967, Midland, Michigan

48641-1967 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: STABLE NON-AQUEOUS LIQUID COMPOSITIONS COMPRISING A CATIONIC POLYMER IN PARTICULATE FORM

(57) Abstract: The need for a stable, compact composition providing improved fabric care benefit, that is also convenient to use, can be met by incorporating a cationic polymer into a non-aqueous composition, using polypropylene glycol. Such compositions have good physical stability, with little or no clumping of the cationic polymer in particulate form.



WO 2015/065809 A1

STABLE NON-AQUEOUS LIQUID COMPOSITIONS COMPRISING A CATIONIC POLYMER IN PARTICULATE FORM

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims benefit of priority from European Patent Application Number EP13190513.5, filed October 28, 2013, which application is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

10 The present invention relates to stable non-aqueous liquid compositions that deliver good fabric care benefit. The invention also relates to a process for stably suspending cationic polymers in non-aqueous liquid compositions.

BACKGROUND OF THE INVENTION

15 Today's consumers desire an easy to use laundry product with improved fabric care benefits, including: improved softness, reduced fabric wrinkles, less mechanical damage during washing, less pills/fuzz, and less colour transfer or fading. Cationic polymers are known in the Art for providing improved fabric care, particularly softness and better fabric feel. Therefore, there is a desire to add these polymers to liquid compositions, including compact compositions, and unit dose
20 liquid laundry articles.

 As liquid laundry compositions become more and more compact, it is desirable to reduce or eliminate those ingredients that do not improve performance, including water. However, certain ingredients, such as cationic polymers are difficult to solubilise when little or no water is present. Also, these ingredients increase the composition viscosity to unacceptable levels at low water
25 concentrations. Various means have been attempted to overcome this problem. Pre-dissolving the cationic polymer with low amounts of water leads to very viscous premixes that are difficult to process. WO 2007/107215 discloses a process whereby, a cationic cellulosic polymer is initially dissolved in water and optionally, a solvent. In addition, it has been discovered that for unit dose articles, cationic polymers can complex with the encapsulating water-soluble or dispersible film,
30 which are generally anionically charged. This leads to reduced film solubility. WO2011/163371 discloses non-aqueous liquid compositions comprising a cationic polymer in particulate form, for unit dose articles and other uses.

 However, a need remains for improved stability of dispersions of cationic polymers in non-aqueous compositions, in addition for improved compatibility with water-soluble or dispersible
35 films.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a non-aqueous liquid composition comprising: a cationic polymer in particulate form; and polypropylene glycol.

The present invention also provides for a process for preparing the non-aqueous liquid composition, characterized in that the process comprises the steps of: providing a cationic polymer dispersion by combining the cationic polymer with the polypropylene glycol; and combining the cationic polymer dispersion with a non-aqueous liquid feed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention solves the problem of providing dispersions of particulate cationic polymers which have improved stability, in addition to improved compatibility with water-soluble or dispersible films.

Polypropylene glycol in the non-aqueous composition, has surprisingly been found to improve the stability of the cationic polymer in particulate form, in the non-aqueous composition. The polypropylene glycol improves the distribution of the cationic polymer particles in the non-aqueous composition, and inhibits cakes or clumps from forming. By using polypropylene glycol to disperse the cationic polymer particles, highly viscous polymer premixes are avoided. A further consequence is that, since the cationic polymer particles remain well suspended and less swollen, they are easier to process and dose.

All percentages, ratios and proportions used herein are by weight percent of the non-aqueous liquid composition. When referring to unit dose articles, all percentages, ratios and proportions used herein are by weight percent of the contents of the unit dose compartment. That is, excluding the weight of the encapsulating material. For multi-compartment unit dose articles, percentages, ratios and proportions used herein, are by weight percent of the contents of the individual unit dose compartment, unless otherwise specified.

"Flowable", as defined herein, refers to a liquid having a viscosity of less than 3000 mPa*s at 20°C, and a shear rate of 20 s⁻¹. Preferably, the viscosity is in the range of from 100 to 2000 mPa*s, more preferably from 500 to 1500 mPa*s, at 20 °C at a shear rate of 20 s⁻¹.

Non-aqueous liquid compositions:

As used herein, "non-aqueous liquid composition" refers to any liquid composition comprising less than 20 %, preferably less than 15 %, more preferably less than 12 %, most preferably less than 8% by weight of water. For instance, containing no additional water beyond what is entrained with other constituent ingredients. The term liquid also includes viscous forms such as gels and pastes. The non-aqueous liquid may include other solids or gases in suitably subdivided form, but excludes forms which are non-liquid overall, such as tablets or granules.

The non-aqueous composition of the present invention may also comprise from 2% to 40 %, more preferably from 5 % to 25 % by weight of additional non-aqueous solvents. That is, in addition to the polypropylene glycol. As used herein, "additional non-aqueous solvent" refers to any organic solvent which contains no amino functional groups, not including polypropylene glycol.

5 Preferred additional non-aqueous solvents include monohydric alcohols; dihydric alcohols; polyhydric alcohols; glycerol; glycols including dipropylene glycol, and polyalkylene glycols such as polyethylene glycol, with the exception of polypropylene glycol; and mixtures thereof. More preferred additional non-aqueous solvents include monohydric alcohols, dihydric alcohols, polyhydric alcohols, glycerol, and mixtures thereof. Highly preferred are mixtures of such solvents, 10 especially mixtures of two or more of the following: lower aliphatic alcohols such as ethanol, propanol, butanol, isopropanol; diols such as 1,2-propanediol or 1,3-propanediol; and glycerol. Also preferred are propanediol and mixtures thereof with diethylene glycol, where the mixture contains no methanol or ethanol. Thus embodiments of non-aqueous liquid compositions of the present invention may include embodiments in which propanediols are used but methanol and ethanol are 15 not used.

Preferable additional non-aqueous solvents are liquid at ambient temperature and pressure (i.e. 21°C and 1 atmosphere), and comprise carbon, hydrogen and oxygen. Additional non-aqueous solvents may be present when preparing a premix, or in the final non-aqueous composition.

20 Cationic polymer in particulate form:

The non-aqueous liquid compositions of the present invention may comprise from 0.01 % to 30 %, preferably from 0.05 % to 25 %, more preferably from 0.1 % to 10 % by weight of the cationic polymer in particulate form. That is, the cationic polymer is insoluble in the non-aqueous liquid composition, or does not fully dissolve in the non-aqueous liquid composition. Preferably, the 25 cationic polymer has a solubility of less than 50wt%, preferably less than 25wt%, more preferably less than 15wt%, even more preferably less than 10wt% most preferably less than 5wt% in the non-aqueous liquid composition, when added at the desired level, at a temperature of 20°C.

The cationic polymer particles preferably have a volume based D90 diameter of less than 300 microns, preferably less than 200 microns, more preferably less than 150 microns. The volume 30 based D90 diameter is defined as 90% of the particles having a volume smaller than the volume of a sphere having the diameter D90. The method for measuring the particle size is given in the Test Methods. The cationic polymer particles are preferably as small as possible. Having smaller particles result in faster dissolution, particularly at lower temperatures, making such particles particularly suitable for providing fabric care benefit during low temperature fabric treatments.

35 Suitable particulate forms include solids that are completely free of water and/or other solvent, but also includes solids that are partially hydrated and/or solvated.

The cationic polymer preferably has a cationic charge density of from 0.005 to 23, more preferably from 0.01 to 12, most preferably from 0.1 to 7 milliequivalents/g, at the pH of the non-aqueous liquid composition. The charge density is calculated by dividing the number of net charges per repeating unit by the molecular weight of the repeating unit. The positive charges could be located

5 on the backbone of the polymer and/or the side chains of polymer.

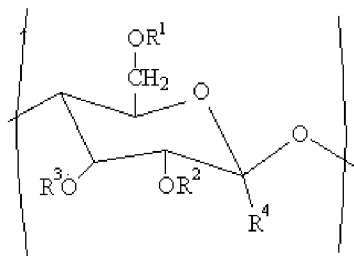
The term "cationic polymer" also includes amphoteric polymers that have a net cationic charge at the pH of the non-aqueous composition. Non-limiting examples of suitable cationic polymers are polysaccharides, proteins and synthetic polymers. Cationic polysaccharides include cationic cellulose derivatives, cationic guar gum derivatives, chitosan and derivatives, and cationic starches.

10 Suitable cationic polysaccharides include cationically modified cellulose, particularly cationic hydroxyethylcellulose and cationic hydroxypropylcellulose. Preferred cationic celluloses for use herein include those which may or may not be hydrophobically-modified, including those having hydrophobic substituent groups, having a molecular weight of from 50,000 to 2,000,000, more preferably from 100,000 to 1,000,000, and most preferably from 200,000 to 800,000. Preferred

15 hydrophobic substituent groups are alkyl substitutions. Alkyl substitution on the anhydroglucose rings of the polymer may range from 0.01% to 10% per glucose unit, preferably from 0.03% to 5%, more preferably from 0.05% to 2% per glucose unit, of the polymeric material.

These cationic materials have repeating substituted anhydroglucose units that correspond to the general Structural Formula I as follows:

20



m

Structural Formula I

wherein:

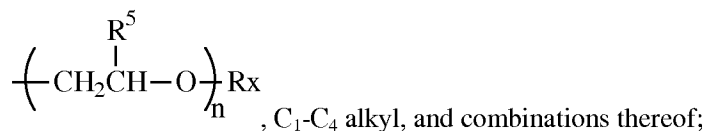
m is an integer from 20 to 10,000

25 Each R4 is H, and R¹, R², R³ are each independently selected from the group consisting of: H; C₁-C₃₂ alkyl; C₁-C₃₂ substituted alkyl, C₅-C₃₂ or C₆-C₃₂ aryl, C₅-C₃₂ or C₆-C₃₂ substituted aryl or C₆-C₃₂

alkylaryl, or C₆-C₃₂ substituted alkylaryl, and

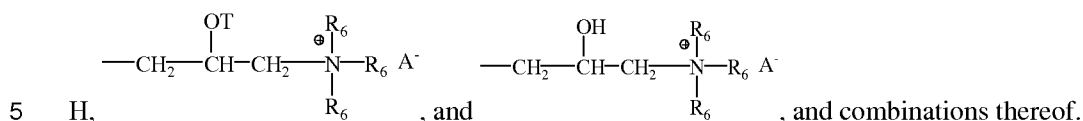
$$\left(\text{CH}_2 \overset{\text{R}^5}{\underset{|}{\text{CH}}} - \text{O} \right)_n \text{R}_x$$

Preferably, R^1 , R^2 , R^3 are each independently selected from the group consisting of: H,



n is an integer selected from 0 to 10 and

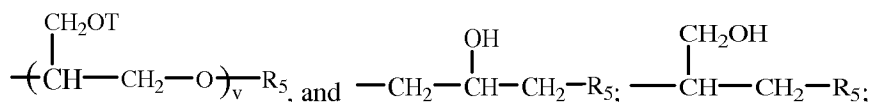
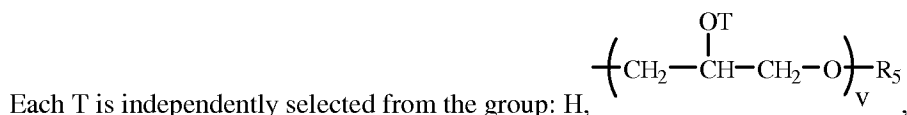
R_x is selected from the group consisting of:



wherein A^- is a suitable anion. Preferably, A^- is selected from the group consisting of: Cl^- , Br^- , I^- , methylsulfate, ethylsulfate, toluene sulfonate, carboxylate, and phosphate;

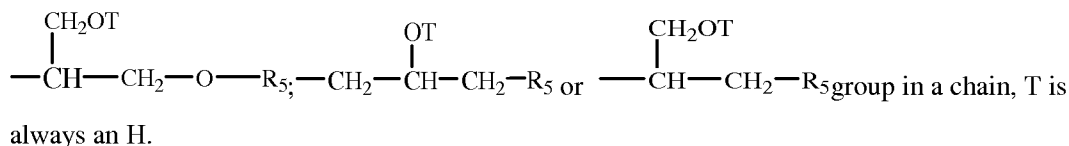
each R_5 is independently selected from the group consisting of: H; C₁-C₃₂ alkyl; C₁-C₃₂ substituted alkyl, C₅-C₃₂ or C₆-C₃₂ aryl, C₅-C₃₂ or C₆-C₃₂ substituted aryl, C₆-C₃₂ alkylaryl, C₆-C₃₂ substituted alkylaryl, and OH. Preferably, each R_5 is selected from the group consisting of: H, C₁-C₃₂ alkyl, and C₁-C₃₂ substituted alkyl. More preferably, R_5 is selected from the group consisting of H, methyl, and ethyl.

Each R_6 is independently selected from the group consisting of: H, C₁-C₃₂ alkyl, C₁-C₃₂ substituted alkyl, C₅-C₃₂ or C₆-C₃₂ aryl, C₅-C₃₂ or C₆-C₃₂ substituted aryl, C₆-C₃₂ alkylaryl, and C₆-C₃₂ substituted alkylaryl. Preferably, each R_6 is selected from the group consisting of: H, C₁-C₃₂ alkyl, and C₁-C₃₂ substituted alkyl.



wherein each v in said polysaccharide is an integer from 1 to 10. Preferably, v is an integer from 1 to 5. The sum of all v indices in each R_x in said polysaccharide is an integer from 1 to 30, more

preferably from 1 to 20, even more preferably from 1 to 10. In the last $\text{---CH}_2\text{---CH}\overset{\text{OT}}{\underset{|}{\text{---}}} \text{---CH}_2\text{---O---R}_5$,

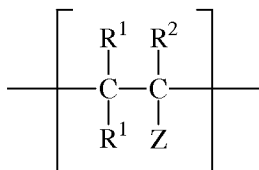


The cationic cellulose may be lightly cross-linked with a dialdehyde, such as glyoxyl, to prevent forming lumps, nodules or other agglomerations when added to water at ambient temperatures.

The cationic cellulose ethers of Structural Formula I likewise include those which are commercially available and further include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers

of the Structural Formula I type include those with the INCI name Polyquaternium 10, such as those sold under the trade names: UCARE Polymer JR 30M, JR 400, JR 125, LR 400 and LK 400 polymers; Polyquaternium 67 such as those sold under the trade name Softcat SKTM, all of which are marketed by The Dow Chemical Company, Midland, Michigan; and Polyquaternium 4 such as those sold under the trade name: Celquat H200 and Celquat L-200, available from National Starch and Chemical Company, Bridgewater, NJ. Other suitable polysaccharides include hydroxyethyl cellulose or hydroxypropylcellulose quaternized with glycidyl C₁₂-C₂₂ alkyl dimethyl ammonium chloride. Examples of such polysaccharides include the polymers with the INCI names Polyquaternium 24 such as those sold under the trade name QUATRISOFT polymer LM- 200 by Amerchol Corporation, Edison, New Jersey. Cationic starches described by D. B. Solarek in Modified Starches, Properties and Uses published by CRC Press (1986) and in U.S. Pat. No. 7,135,451, col. 2, line 33 – col. 4, line 67. Suitable cationic galactomannans include cationic guar gums or cationic locust bean gum. An example of a cationic guar gum is a quaternary ammonium derivative of Hydroxypropyl Guar such as those sold under the trade name: Jaguar C13 and Jaguar Excel available from Rhodia, Inc of Cranbury NJ and N-Hance by Aqualon, Wilmington, DE.

A synthetic cationic polymer may also be useful as the cationic polymer. Synthetic polymers include synthetic addition polymers of the general structure:



Structural Formula II

wherein each R¹ may be independently: hydrogen, C₁-C₁₂ alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted benzyl, -OR_a, or -C(O)OR_a wherein R_a may be selected from the group consisting of: hydrogen, C₁-C₂₄ alkyl, and combinations thereof. R¹ is preferably: hydrogen, C₁-C₄ alkyl, or -OR_a, or -C(O)OR_a;

wherein each R² may be independently selected from the group consisting of: hydrogen, hydroxyl, halogen, C₁-C₁₂ alkyl, -OR_a, substituted or unsubstituted phenyl, substituted or unsubstituted benzyl, carbocyclic, heterocyclic, and combinations thereof. R² is preferably selected from the group consisting of: hydrogen, C₁-C₄ alkyl, and combinations thereof.

Each Z may be independently: hydrogen, halogen; linear or branched C₁-C₃₀ alkyl, nitrilo, N(R₃)₂ - C(O)N(R₃)₂; -NHCHO (formamide); -OR³, -O(CH₂)_nN(R³)₂, -O(CH₂)_nN⁺(R³)₃X⁻, -C(O)OR⁴; - C(O)N-(R³)₂; -C(O)O(CH₂)_nN(R³)₂, -C(O)O(CH₂)_nN⁺(R³)₃X⁻, -OCO(CH₂)_nN(R³)₂, - OCO(CH₂)_nN⁺(R³)₃X⁻, -C(O)NH-(CH₂)_nN(R³)₂, -C(O)NH(CH₂)_nN⁺(R³)₃X⁻, -(CH₂)_nN(R³)₂, - (CH₂)_nN⁺(R³)₃X⁻.

Each R_3 may be independently selected from the group consisting of: hydrogen, C_1 - C_{24} alkyl, C_2 - C_8 hydroxyalkyl, benzyl, substituted benzyl, and combinations thereof;

Each R_4 may be independently selected from the group consisting of: hydrogen, C_1 - C_{24} alkyl,

$-(CH_2-\overset{\overset{R_5}{|}}{CH}-O)_{\text{m}}$, and combinations thereof.

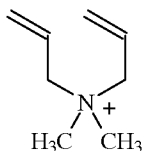
- 5 X may be a water soluble anion. n may be from 1 to 6.

R_5 may be independently selected from the group consisting of: hydrogen, C_1 - C_6 alkyl, and combinations thereof.

- Z, from Structural Formula II, may also be selected from the group consisting of: non-aromatic nitrogen heterocycles containing a quaternary ammonium ion, heterocycles containing an N-oxide moiety, aromatic nitrogens containing heterocycles wherein one or more of the nitrogen atoms may be quaternized; aromatic nitrogen-containing heterocycles wherein at least one nitrogen may be an N-oxide, and combinations thereof. Non-limiting examples of addition polymerizing monomers comprising a heterocyclic Z unit includes 1-vinyl-2-pyrrolidinone, 1-vinylimidazole, quaternized vinyl imidazole, 2-vinyl-1,3-dioxolane, 4-vinyl-1-cyclohexene 1,2-epoxide, and 2-vinylpyridine, 2-vinylpyridine N-oxide, 4-vinylpyridine 4-vinylpyridine N-oxide.

A non-limiting example of a Z unit which can be made to form a cationic charge in situ, may be the -NHCHO unit, formamide. The formulator can prepare a polymer, or co-polymer, comprising formamide units some of which are subsequently hydrolyzed to form vinyl amine equivalents.

- 20 The polymers or co-polymers may also contain one or more cyclic polymer units derived from cyclically polymerizing monomers. An example of a cyclically polymerizing monomer is dimethyl diallyl ammonium having the formula:



- Suitable copolymers may be made from one or more cationic monomers selected from the group consisting of N,N-dialkylaminoalkyl methacrylate, N,N-dialkylaminoalkyl acrylate, N,N-dialkylaminoalkyl acrylamide, N,N-dialkylaminoalkylmethacrylamide, quaternized N,N-dialkylaminoalkyl methacrylate, quaternized N,N-dialkylaminoalkyl acrylate, quaternized N,N-dialkylaminoalkyl acrylamide, quaternized N,N-dialkylaminoalkylmethacrylamide, vinylamine and its derivatives, allylamine and its derivatives, vinyl imidazole, quaternized vinyl imidazole and diallyl dialkyl ammonium chloride and combinations thereof, and optionally a second monomer selected from the group consisting of acrylamide, N,N-dialkyl acrylamide, methacrylamide, N,N-dialkylmethacrylamide, C_1 - C_{12} alkyl acrylate, C_1 - C_{12} hydroxyalkyl acrylate, polyalkylene glycol acrylate, C_1 - C_{12} alkyl methacrylate, C_1 - C_{12} hydroxyalkyl methacrylate, polyalkylene glycol

methacrylate, vinyl acetate, vinyl alcohol, vinyl formamide, vinyl acetamide, vinyl alkyl ether, vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and derivatives, acrylic acid, methacrylic acid, maleic acid, vinyl sulfonic acid, styrene sulfonic acid, acrylamidopropylmethane sulfonic acid (AMPS) and their salts, and combinations thereof. The polymer may optionally be cross-linked. Suitable

5 crosslinking monomers include ethylene glycoldiacrylate, divinylbenzene, butadiene.

In certain embodiments, the synthetic polymers are: poly(acrylamide-co-diallyldimethylammonium chloride), poly(acrylamide-methacrylamidopropyltrimethyl ammonium chloride), poly(acrylamide-co-N,N-dimethyl aminoethyl methacrylate), poly(acrylamide-co-N,N-dimethyl aminoethyl methacrylate), poly(hydroxyethylacrylate-co-dimethyl aminoethyl

10 methacrylate), poly(hydroxypropylacrylate-co-dimethyl aminoethyl methacrylate), poly(hydroxypropylacrylate-co-methacrylamidopropyltrimethylammonium chloride), poly(acrylamide-co-diallyldimethylammonium chloride-co-acrylic acid), poly(acrylamide-methacrylamidopropyltrimethyl ammonium chloride-co-acrylic acid). Examples of other suitable synthetic polymers are Polyquaternium-1, Polyquaternium-5, Polyquaternium-6, Polyquaternium-7,

15 Polyquaternium-8, Polyquaternium-11, Polyquaternium-14, Polyquaternium-22, Polyquaternium-28, Polyquaternium-30, Polyquaternium-32 and Polyquaternium-33. Other cationic polymers include polyethyleneamine and its derivatives and polyamidoamine-epichlorohydrin (PAE) Resins. In one aspect, the polyethylene derivative may be an amide derivative of polyethylenimine sold under the trade name Lupasol SK. Also included are alkoxyated polyethylenimine; alkyl polyethylenimine

20 and quaternized polyethylenimine. These polymers are described in Wet Strength resins and their applications edited by L. L. Chan, TAPPI Press (1994). The weight-average molecular weight of the polymer will generally be from 10,000 to 5,000,000, or from 100,000 to 200,000, or from 200,000 to 1,500,000 Daltons, as determined by size exclusion chromatography relative to polyethylene oxide standards with RI detection. The mobile phase used is a solution of 20% methanol in 0.4M

25 MEA, 0.1 M NaNO₃, 3% acetic acid on a Waters Linear Ultrahydrogel column, 2 in series. Columns and detectors are kept at 40°C. Flow is set to 0.5 mL/min.

Polypropylene glycol:

The non-aqueous composition of the present invention comprises polypropylene glycol.

30 The non-aqueous liquid composition may comprise from 0.05 % to 98 %, preferably from 0.5 % to 75 %, more preferably from 3 % to 68 % by weight of polypropylene glycol. Surprisingly, it has been found that polypropylene glycol greatly improves the physical stability of the cationic polymer particulates in the non-aqueous composition. It is believed that the polypropylene glycol inhibits the agglomeration of the cationic polymer particles, by limiting the solvation, and hence swelling of the

35 particles. Moreover, since the particles are less swollen, they are less visible, even when they deposit on a water-soluble film which is used to form a unit-dose article. Furthermore, even when

they do deposit on such water-soluble films, they are less able to interact with the water-soluble film, since they are less solvated. As a result, there is less impact on the dissolution of the water-soluble film, such as during a wash cycle.

Any agglomerates that may form over time, are easily redistributed by gentle shaking.

- 5 Preferably, the polypropylene glycol has a molecular weight of from 208 g/mol to 4000 g/mol, more preferably from 208 g/mol to 2000 g/mol, even more preferably from 250 g/mol to 700 g/mol.

The strength of any agglomerates that may form is further reduced by adding spacer particles. Suitable spacer particles may have an volume based D90 diameter of less than 5 microns, preferably from 0.1 microns to 1 micron. The spacer particles may be polymeric or non-polymeric.

- 10 Suitable non-polymeric spacer particles include mica. Suitable polymeric spacer particles include those comprising a polymer and/or a copolymer. Preferably, the spacer particles are anionically charged, such as those comprising a polyacrylate polymer or copolymer. It is believed that the anionic charge attracts the spacer particle to the cationic polymer particles. The non-aqueous composition of the present invention may comprise from 0.1 % to 30 %, preferably from 0.5 percent
15 to 15 % by weight of the spacer particles.

- Any present agglomerates of the cationic polymer particles may also be weakened by the presence of soluble cations and/or polyvalent anions. While polyvalent cations, particularly those having the charges derived from different charged groups are preferred, even monovalent cations have been shown to provide a benefit. It is believed that the cations form bilayers that are able to reduce the
20 attraction between the cationic polymer particles. Suitable single species polyvalent cations include the cations of magnesium and calcium. Suitable cationic surfactants are preferably water-soluble, but can also be water-dispersible or water-insoluble. Such cationic surfactants have at least one quaternized nitrogen and at least one long-chain hydrocarbyl group. Compounds comprising two, three or even four long-chain hydrocarbyl groups are also included. Examples include
25 alkyltrimethylammonium salts, such as C12 alkyltrimethylammonium chloride, or their hydroxyalkyl substituted analogues. The present invention may comprise from 1% or more by weight of the cationic surfactant. Amphoteric surfactants, particularly those that have a net cationic charge at the pH of the non-aqueous composition, are also useful cations for the present invention. Suitable polyvalent anions include: Citric Acid; Diethylene triamine pentaacetic acid (DTPA); 1-
30 hydroxyethane 1,1-diphosphonic acid (HEDP); Maleic acid; Polyacrylates; Polyacrylic/maleic acid copolymers; succinic acid, and mixtures thereof. The non-aqueous composition may comprise from 0.1 % to 30 %, preferably from 0.5 to 15 % by weight of the cation and/or polyvalent anion.

Laundering adjuncts:

- The non-aqueous liquid compositions of the present invention may include conventional
35 laundry detergent ingredients selected from the group consisting of: anionic and nonionic surfactants; additional surfactants; enzymes; enzyme stabilizers; cleaning polymers, including:

amphiphilic alkoxyated grease cleaning polymers, clay soil cleaning polymers, soil release polymers, and soil suspending polymers; bleaching systems; optical brighteners; hueing dyes; particulate material; perfume and other odour control agents; hydrotropes; suds suppressors; fabric care benefit agents; pH adjusting agents; dye transfer inhibiting agents; preservatives; non-fabric substantive dyes and mixtures thereof. Some of the optional ingredients which can be used are described in greater detail as follows:

Anionic and nonionic surfactants: Non-aqueous liquid compositions of the present invention may comprise from 1% to 70%, preferably from 10% to 50%, and more preferably from 15% to 45% by weight of an anionic and/or nonionic surfactant.

The non-aqueous liquid compositions of the present invention preferably comprise from 1 to 70 %, more preferably from 5 to 50 % by weight of one or more anionic surfactants. Preferred anionic surfactant are selected from the group consisting of: C11-C18 alkyl benzene sulfonates, C10-C20 branched-chain and random alkyl sulfates, C10-C18 alkyl ethoxy sulfates, mid-chain branched alkyl sulfates, mid-chain branched alkyl alkoxy sulfates, C10-C18 alkyl alkoxy carboxylates comprising 1-5 ethoxy units, modified alkylbenzene sulfonate, C12-C20 methyl ester sulfonate, C10-C18 alpha-olefin sulfonate, C6-C20 sulfosuccinates, fatty acids, and mixtures thereof. However, by nature, every anionic surfactant known in the art of detergent compositions may be used, such as those disclosed in "Surfactant Science Series", Vol. 7, edited by W. M. Linfield, Marcel Dekker. However, the compositions of the present invention preferably comprise at least one sulphonic acid surfactant, such as a linear alkyl benzene sulphonic acid, or the water-soluble salt forms.

Anionic sulfonate or sulfonic acid surfactants suitable for use herein include the acid and salt forms of linear or branched C5-C20, more preferably C10-C16, most preferably C11-C13 alkylbenzene sulfonates, C5-C20 alkyl ester sulfonates, C6-C22 primary or secondary alkane sulfonates, C5-C20 sulfonated polycarboxylic acids, and mixtures thereof. The aforementioned surfactants can vary widely in their 2-phenyl isomer content. Anionic sulphate salts suitable for use in compositions of the invention include: primary and secondary alkyl sulphates, having a linear or branched alkyl or alkenyl moiety having from 9 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms; beta-branched alkyl sulphate surfactants; and mixtures thereof. Mid-chain branched alkyl sulphates or sulfonates are also suitable anionic surfactants for use in the compositions of the invention. Preferred are the C5-C22, preferably C10-C20 mid-chain branched alkyl primary sulphates. When mixtures are used, a suitable average total number of carbon atoms for the alkyl moieties is preferably within the range of from 14.5 to 17.5. Preferred mono-methyl-branched primary alkyl sulphates are selected from the group consisting of the 3-methyl to 13-methyl pentadecanol sulphates, the corresponding hexadecanol sulphates, and mixtures thereof. Dimethyl derivatives or other biodegradable alkyl sulphates having light branching can similarly be used.

Other suitable anionic surfactants for use herein include fatty methyl ester sulphonates and/or alkyl ethoxy sulphates (AES) and/or alkyl polyalkoxylated carboxylates (AEC).

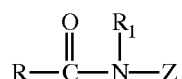
Any fatty acid is suitable for use herein, including but not limited to lauric, myristic, palmitic stearic, oleic, linoleic, linolenic acid, and mixtures thereof. The fatty acid is preferably
 5 selected from those which are flowable at less than 30°C. Naturally obtainable fatty acids, which are usually complex mixtures, are also suitable (such as tallow, coconut, and palm kernel fatty acids). A preferred fatty acid is palm kernel fatty acid. Furthermore, such fatty acids provide a builder benefit, and after neutralization, a detergency benefit. The amount of fatty acid can be in the range of from 0.1% to 30%, preferably from 1% to 20%, more preferably from 3 to 15%, by weight
 10 of the composition.

Mixtures of anionic surfactants can be used, for example mixtures of alkylbenzenesulphonates and AES.

The anionic surfactants are typically present in the form of their salts with alkanolamines or alkali metals such as sodium and potassium. Preferably, the anionic surfactants are neutralized with
 15 alkanolamines, such as monoethanolamine or triethanolamine, and are fully soluble in the non-aqueous liquid composition.

The non-aqueous liquid compositions of the present invention may include from 1 to 70 %, preferably from 5 to 50 % by weight of a nonionic surfactant. Suitable nonionic surfactants include, but are not limited to C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl
 20 ethoxylates, C6-C12 alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxylates/propoxylates), block alkylene oxide condensate of C6-C12 alkyl phenols, alkylene oxide condensates of C8-C22 alkanols and ethylene oxide/propylene oxide block polymers (Pluronic®-BASF Corp.), glycereth cocoate, alkyl polyglucosides, as well as semi polar nonionics (e.g., amine oxides and phosphine oxides). An extensive disclosure of suitable nonionic surfactants
 25 can be found in U.S. Pat. 3,929,678.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 are also useful nonionic surfactants for compositions of the invention. Also suitable are alkyl polyglucoside surfactants. In some embodiments, suitable nonionic surfactants include those of the formula $R_1(OC_2H_4)_nOH$, wherein R1 is a C10-C16 alkyl group or a C8-C12 alkyl phenyl group, and n is from 3 to 80. In
 30 some embodiments, the nonionic surfactants may be condensation products of C12-C15 alcohols with from 5 to 20 moles of ethylene oxide per mole of alcohol, e.g., C12-C13 alcohol condensed with 6.5 moles of ethylene oxide per mole of alcohol. Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:



wherein R is a C9-C17 alkyl or alkenyl, R1 is a methyl group and Z is glycidyl derived from a reduced sugar or alkoxyated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide.

Additional Surfactants: The non-aqueous liquid compositions of the present invention may
5 comprise additional surfactant selected from the group consisting: anionic, cationic, nonionic, amphoteric and/or zwitterionic surfactants and mixtures thereof.

Amphoteric deterative surfactants suitable for use in the composition include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from
10 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulphonate, sulphate, phosphate, or phosphonate. Suitable amphoteric deterative surfactants for use in the present invention include, but are not limited to: cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic deterative surfactants suitable for use in non-aqueous liquid compositions are
15 well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulphonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulphate, phosphate or phosphonate. Zwitterionics such as betaines are also suitable for this invention. Furthermore,
20 amine oxide surfactants having the formula: $R(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2 \cdot qH_2O$ are also useful in compositions of the present invention. R is a relatively long-chain hydrocarbyl moiety which can be saturated or unsaturated, linear or branched, and can contain from 8 to 20, preferably from 10 to 16 carbon atoms, and is more preferably C12-C16 primary alkyl. R' is a short-chain moiety preferably selected from hydrogen, methyl and $-CH_2OH$. When $x+y+z$ is different from 0, EO is
25 ethyleneoxy, PO is propyleneoxy and BO is butyleneoxy. Amine oxide surfactants are illustrated by C12-C14 alkyldimethyl amine oxide.

Non-limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Pat. Nos. 3,929,678,
30 2,658,072; 2,438,091; 2,528,378.

Enzymes: The non-aqueous liquid compositions of the present invention may comprise from 0.0001 % to 8 % by weight of a deterative enzyme which provides cleaning performance and/or fabric care benefits. Such compositions preferably have a composition pH of from 6 to 10.5. Suitable enzymes can be selected from the group consisting of: lipase, protease, amylase, cellulase,
35 mannanase, pectate lyase, xyloglucanase, and mixtures thereof. A preferred enzyme combination

comprises a cocktail of conventional detergent enzymes such as lipase, protease, cellulase and amylase. Detergent enzymes are described in greater detail in U.S. Patent No. 6,579,839.

Enzyme Stabilizers: Enzymes can be stabilized using any known stabilizer system such as calcium and/or magnesium compounds, boron compounds and substituted boric acids, aromatic borate esters, peptides and peptide derivatives, polyols, low molecular weight carboxylates, relatively hydrophobic organic compounds [e.g. certain esters, dialkyl glycol ethers, alcohols or alcohol alkoxylates], alkyl ether carboxylate in addition to a calcium ion source, benzamidine hypochlorite, lower aliphatic alcohols and carboxylic acids, N,N-bis(carboxymethyl) serine salts, (meth)acrylic acid-(meth)acrylic acid ester copolymer and PEG; lignin compound, polyamide oligomer, glycolic acid or its salts, poly hexamethylene biguanide or N,N-bis-3-amino-propyl-dodecyl amine or salt, sorbitol, and mixtures thereof.

Fabric Care Benefit Agents: The non-aqueous composition may comprise from 1 % to 15 %, more preferably from 2 % to 7 %, by weight of a fabric care benefit agent. "Fabric care benefit agent", as used herein, refers to any material that can provide fabric care benefits. Non-limiting examples of fabric care benefits include, but are not limited to: fabric softening, colour protection, colour restoration, pill/fuzz reduction, anti-abrasion and anti-wrinkling. Non-limiting examples of fabric care benefit agents include: silicone derivatives, such as polydimethylsiloxane and amino-functional silicones; oily sugar derivatives; dispersible polyolefins; polymer latexes; cationic surfactants and combinations thereof.

Cleaning Polymers: The non-aqueous liquid compositions herein, may contain from 0.01 % to 20 %, preferably from 0.05 % to 15 %, more preferably from 0.1 % to 10 % by weight of cleaning polymers, that provide for broad-range soil cleaning of surfaces and fabrics. Any suitable cleaning polymer may be of use. Useful cleaning polymers are described in US 2009/0124528A1. Non-limiting examples of useful categories of cleaning polymers include: amphiphilic alkoxylated grease cleaning polymers; clay soil cleaning polymers; soil release polymers; and soil suspending polymers. Other anionic polymers, useful for improving soil cleaning include: non-silicone-containing polymers of natural origin, but also of synthetic origin. Suitable anionic non-silicone-containing polymers may be selected from the group consisting of xanthan gum, anionic starch, carboxymethyl guar, carboxymethyl hydroxypropyl guar, carboxy methyl cellulose and ester modified carboxymethyl cellulose, N-carboxyalkyl chitosan, N-carboxyalkyl chitosan amides, pectin, carrageenan gum, chondroitin sulfate, galactomanans, hyaluronic acid-, and alginic acid-based polymers, and derivatives thereof and mixtures thereof. More preferably, the anionic non-silicone-containing polymer may be selected from carboxymethyl guar, carboxymethyl hydroxypropyl guar, carboxymethyl cellulose and xanthan gum, and derivatives and mixtures thereof. Preferred anionic non-silicone-containing polymers include those commercially available

from CPKelco, sold under the tradename of Kelzan® RD and from Aqualon, sold under the tradename of Galactosol® SP722S, Galactosol® 60H3FD, and Galactosol® 70H4FD.

Optical brighteners: These are also known as fluorescent whitening agents for textiles. Preferred levels are from 0.001 % to 2 % by weight of the non-aqueous liquid composition. Suitable brighteners are disclosed in EP 686691B and include hydrophobic as well as hydrophilic types. Brightener 49 is preferred for use in the present invention.

Hueing dyes: Hueing dyes or fabric shading dyes are useful laundering adjuncts in non-aqueous liquid compositions. Suitable dyes include blue and/or violet dyes having a hueing or shading effect. See, for example, WO 2009/087524 A1, WO2009/087034A1 and references therein. Recent developments that are suitable for the present invention include sulfonated phthalocyanine dyes having a zinc or aluminium central atom. The non-aqueous liquid compositions herein may comprise from 0.00003 % to 0.1 %, preferably from 0.00008 % to 0.05 % by weight of the fabric hueing dye.

Particulate material: The non-aqueous composition may include additional particulate material such as clays, suds suppressors, encapsulated oxidation-sensitive and/or thermally sensitive ingredients such as perfumes (perfume microcapsules), bleaches and enzymes; or aesthetic adjuncts such as pearlescent agents including mica, pigment particles, or the like. Suitable levels are from 0.0001 % to 10 %, or from 0.1 % to 5 % by weight of the non-aqueous composition.

Perfume and other odour control agents: In preferred embodiments, the non-aqueous composition comprises a free and/or micro-encapsulated perfume. If present, the free perfume is typically incorporated at a level from 0.001 % to 10 %, preferably from 0.01 % to 5 %, more preferably from 0.1 % to 3 % by weight of the non-aqueous composition.

If present, the perfume microcapsule is formed by at least partially surrounding the perfume raw materials with a wall material. Preferably, the microcapsule wall material comprises: melamine crosslinked with formaldehyde, polyurea, urea crosslinked with formaldehyde or urea crosslinked with glutaraldehyde. Suitable perfume microcapsules and perfume nanocapsules include those described in the following references: US 2003215417 A1; US 2003216488 A1; US 2003158344 A1; US 2003165692 A1; US 2004071742 A1; US 2004071746 A1; US 2004072719 A1; US 2004072720 A1; EP 1393706 A1; US 2003203829 A1; US 2003195133 A1; US 2004087477 A1; US 20040106536 A1; US 6645479; US 6200949; US 4882220; US 4917920; US 4514461; US RE 32713; US 4234627.

In other embodiments, the non-aqueous composition comprises odour control agents such as uncomplexed cyclodextrin, as described in US 5,942,217. Other suitable odour control agents include those described in: US 5,968,404, US 5,955,093, US 6,106,738, US 5,942,217, and US 6,033,679.

Hydrotropes: The non-aqueous liquid composition of the present invention typically comprises a hydrotrope in an effective amount, preferably up to 15%, more preferably from 1 % to 10 %, most preferably from 3 % to 6 % by weight, so that the compositions are readily dispersed in water. Suitable hydrotropes for use herein include anionic-type hydrotropes, particularly sodium, potassium, and ammonium xylene sulfonate, sodium, potassium and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof, as disclosed in US 3,915,903.

Multivalent water-soluble organic builder and/or chelant: The non-aqueous liquid compositions of the present invention may comprise from 0.6 % to 25 %, preferably from 1 % to 20 %, more preferably from 2 % to 7 % by weight of the multivalent water-soluble organic builder and/or chelants. Water-soluble organic builders provide a wide range of benefits including sequestration of calcium and magnesium (improving cleaning in hard water), provision of alkalinity, transition metal ion complexation, metal oxide colloid stabilisation, and provision of substantial surface charge for peptisation and suspension of other soils. Chelants may selectively bind transition metals (such as iron, copper and manganese) which impact stain removal and the stability of bleach ingredients, such as organic bleach catalysts, in the wash solution. Preferably, the multivalent water-soluble organic builder and/or chelants of the present invention are selected from the group consisting of: MEA citrate, citric acid, aminoalkylenepoly(alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates, and nitrilotrimethylene, phosphonates, diethylene triamine penta (methylene phosphonic acid) (DTPMP), ethylene diamine tetra(methylene phosphonic acid) (DDTMP), hexamethylene diamine tetra(methylene phosphonic acid), hydroxy-ethylene 1,1 diphosphonic acid (HEDP), hydroxyethane dimethylene phosphonic acid, ethylene diamine di-succinic acid (EDDS), ethylene diamine tetraacetic acid (EDTA), hydroxyethylethylenediamine triacetate (HEDTA), nitrilotriacetate (NTA), methylglycinediacetate (MGDA), iminodisuccinate (IDS), hydroxyethyliminodisuccinate (HIDS), hydroxyethyliminodiacetate (HEIDA), glycine diacetate (GLDA), diethylene triamine pentaacetic acid (DTPA), and mixtures thereof.

External structuring system: The physical stability of the cationic polymer particulates in the non-aqueous liquid composition can be further improved if the non-aqueous liquid composition also comprises an external structurant. An external structuring system is a compound or mixture of compounds which provide either a sufficient yield stress or low shear viscosity to stabilize the non-aqueous liquid compositions independently from, or extrinsic from, the structuring effect of any deterative surfactants in the composition. The non-aqueous liquid composition may comprise from 0.01 % to 10 %, preferably from 0.1 % to 4 % by weight of an external structuring system, on an active basis. Suitable external structuring systems include non-polymeric crystalline, hydroxy-functional structurants, polymeric structurants, or mixtures thereof.

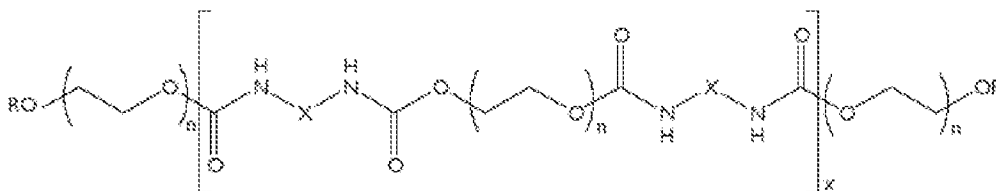
Preferably, the external structurant system imparts a high shear viscosity at 20 s^{-1} , at 20°C , of from 1 to 3000 cps, and a viscosity at low shear (at 0.05 s^{-1} at 20°C) of greater than 5000 cps. The viscosity is measured using an AR 550 rheometer, from TA instruments, using a plate steel spindle with a 40 mm diameter and a gap size of $1000\text{ }\mu\text{m}$. The high shear viscosity at 20 s^{-1} can be obtained from a logarithmic shear rate sweep from 0.1 s^{-1} to 1200 s^{-1} in 3 minutes time at 20°C . The low shear viscosity is measured over a period of 3 minutes at a fixed shear rate ("Peak Hold") of 0.05 s^{-1} at 20°C .

The external structuring system may comprise a non-polymeric crystalline, hydroxyl functional structurant. Such non-polymeric crystalline, hydroxyl functional structurants generally comprise a crystallisable glyceride which can be pre-emulsified to aid dispersion into the final non-aqueous composition. Preferred crystallisable glycerides include hydrogenated castor oil or "HCO", and derivatives thereof, provided that it is capable of crystallizing in the non-aqueous composition. Other embodiments of suitable external structuring systems may comprise a naturally derived and/or synthetic polymeric structurant. Examples of suitable naturally derived polymeric structurants include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives, and mixtures thereof. Suitable polysaccharide derivatives include: pectine, alginate, arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum, and mixtures thereof. Examples of suitable synthetic polymeric structurants include: polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes (HEUR), hydrophobically modified alkali swellable emulsions (HASE), and mixtures thereof.

Preferred polymeric structurants can be selected from the group consisting of: hydrophobically-modified ethoxylated urethanes (HEUR); hydrophobically modified alkali swellable emulsion (HASE) polymers, and mixtures thereof. HEUR and HASE polymeric structurants are typically used for structuring in aqueous compositions. However, such polymers have been found to be particularly effective for suspending the cationic polymer, in particulate form, in the non-aqueous composition. HEUR polymeric structurants are water-soluble polymers, having hydrophobic end-groups, comprising blocks of ethylene glycol units, propylene glycol units, and mixtures thereof, in addition to urethane units.

The HEUR polymeric structurants preferably has a backbone comprising one or more polyoxyalkylene segments greater than 10 oxyalkylene units in length. The HEUR polymeric structurant is preferably a hydrophobically modified polyurethane polyether comprising the reaction product of a dialkylamino alkanol with a multi-functional isocyanate, a polyether diol, and optionally a polyether triol. Preferably, the polyether diol has a weight average molecular weight between 2,000 and 12,000, preferably between 6,000 and 10,000.

Preferred HEUR polymeric structurants can have the following structure:



wherein:

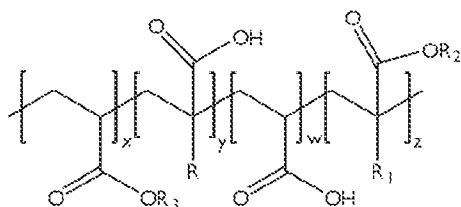
R is an alkyl chain, preferably a C6-C24 alkyl chain, more preferably a C12-C18 alkyl chain, n is preferably from 25 to 400, preferably from 50 to 250, more preferably from 75 to 180, X can be any suitable linking group.

Suitable HEUR polymeric structurants can have a molecular weight of from 1,000 to 1,000,000, more preferably from 15,000 to 50,000 g/mol. An example of a suitable HEUR polymeric structurant is ACUSOL™ 880, sold by DOW.

It is believed that HEUR polymeric structurants thicken via an associative mechanism, wherein the hydrophobic parts of HEUR polymers build up associations with other hydrophobes present in the composition, such as the cationic polymers in particulate form.

HASE polymers are typically synthesized by free-radical emulsion polymerization of varying mixtures of hydrophilic monomers such as acrylic acid, methacrylic acid, or maleic anhydride, lipophilic monomers such as ethyl acrylate, butyl acrylate, or methyl methacrylate, and associative monomers such as long chain alkyl (C8 to C22) acrylates or styrenic derivatives.

Preferred HASE polymeric structurants can have the following structure:



wherein:

R is preferably H or an alkyl group. When R is an alkyl group, R is preferably a C1-C6 alkyl group, more preferably a C1 to C2 alkyl group. R is preferably a C1 alkyl group.

R₁ is preferably H or an alkyl group. When R₁ is an alkyl group, R is preferably a C1-C6 alkyl group, more preferably a C1 to C2 alkyl group. R₁ is preferably a C1 alkyl group.

R₂ is any suitable hydrophobic group, such as a C4-C24 alkyl group, more preferably a C8-C20 alkyl group. R₂ can also be alkoxyated. Preferably, R₂ is ethoxyated, propoxyated, and combinations thereof. More preferably R₂ is ethoxyated. When alkoxyated, R₂ can be alkoxyated to a degree of from 1 to 60, preferably from 10 to 50.

R₃ is preferably H or an alkyl group. When R₃ is an alkyl group, R₃ is preferably a C1-C6 alkyl group, more preferably a C1 to C3 alkyl group. R₃ is preferably a C2 alkyl group.

The repeating units comprising R, R₁, R₂, and R₃ can be in any suitable order, or even randomly distributed through the polymer chain.

5 Suitable HASE polymeric structurants can have a molecular weight of from 50,000 to 500,000 g/mol, preferably from 80,000 to 400,000 g/mol, more preferably from 100,000 to 300,000 g/mol.

The ratio of x:y can be from 1:20 to 20:1, preferably from 1:10 to 10:1, more preferably from 1:5 to 5:1. The ratio of x:w can be from 1:20 to 20:1, preferably from 1:10 to 10:1, more preferably from 1:5 to 5:1. The ratio of x:z can be from 1:1 to 500:1, preferably from 2:1 to 250:1,
10 more preferably from 25:1 to 75:1.

An example of a suitable HASE polymeric structurants are ACUSOL™ 801S, ACUSOL™805S, ACUSOL™ 820, ACUSOL™ 823, sold by DOW.

HASE polymeric structurants are believed to structure by a combination of polyelectrolytic chain expansion and through association of the hydrophobe groups, present in the HASE polymeric
15 structurant, with other hydrophobes present in the composition, such as the cationic polymers in particulate form.

Methods of making such HASE polymeric structurants are described in U.S. Patent No. 4,514,552, U.S. Patent No. 5,192,592, British Patent No. 870,994, and U.S. Patent No. 7,217,443.

The non-aqueous liquid composition can comprise further structurants, such as
20 hydrogenated castor oil.

The unit dose article

Non-aqueous liquid compositions of the present invention may be comprised in unit dose articles, having at least one liquid filled compartment. A liquid-filled compartment refers to a partition of the unit dose article comprising a liquid capable of wetting a fabric e.g., clothing. Such
25 unit dose articles comprise, in single, easy to use dosage form: a cationic polymer in particulate form, stably suspended in a non-aqueous composition which further comprises polypropylene glycol, encapsulated in a water-soluble or dispersible film.

The unit dose article can be of any form, shape and material which is suitable for holding the non-aqueous composition, i.e. without allowing the release of the non-aqueous composition,
30 and any additional component, from the unit dose article prior to contact of the unit dose article with water. The exact execution will depend, for example, on the type and amount of the compositions in the unit dose article, the number of compartments in the unit dose article, and on the characteristics required from the unit dose article to hold, protect and deliver or release the compositions or components.

35 The unit dose article comprises a water-soluble or dispersible film which fully encloses at least one inner volume, comprising the non-aqueous composition. The unit dose article may

optionally comprise additional compartments comprising non-aqueous liquid and/or solid components. Alternatively, any additional solid component may be suspended in a liquid-filled compartment. A multi-compartment unit dose form may be desirable for such reasons as: separating chemically incompatible ingredients; or where it is desirable for a portion of the ingredients to be released into the wash earlier or later.

It may be preferred that any compartment which comprises a liquid component also comprises an air bubble. The air bubble may have a volume of less than 50%, preferably less than 40%, more preferably less than 30%, more preferably less than 20%, most preferably less than 10% of the volume space of said compartment. Without being bound by theory, it is believed that the presence of the air bubble increases the tolerance of the unit dose article to the movement of the liquid component within the compartment, thus reducing the risk of the liquid component leaking from the compartment.

Water-soluble or dispersible film: The water-soluble or dispersible film typically has a solubility of at least 50%, preferably at least 75%, more preferably at least 95%. The method for determining water-solubility of the film is given in the Test Methods. The water-soluble or dispersible film typically has a dissolution time of less than 100 seconds, preferably less than 85 seconds, more preferably less than 75 seconds, most preferably less than 60 seconds. The method for determining the dissolution time of the film is given in the Test Methods.

Preferred films are polymeric materials, preferably polymers which are formed into a film or sheet. The film can be obtained by casting, blow-moulding, extrusion or blow extrusion of the polymer material, as known in the art. Preferably, the water-soluble or dispersible film comprises: polymers, copolymers or derivatives thereof, including polyvinyl alcohols (PVA), polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum gum and carrageenan. More preferably, the water-soluble or dispersible film comprises: polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates. Most preferably, the water-soluble or dispersible film comprises: polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC). Preferably, the level of polymer or copolymer in the film is at least 60 % by weight. The polymer or copolymer preferably has a weight average molecular weight of from 1000 to 1,000,000, more preferably from 10,000 to 300,000, even more preferably from 15,000 to 200,000, and most preferably from 20,000 to 150,000.

Copolymers and mixtures of polymers can also be used. This may in particular be beneficial to control the mechanical and/or dissolution properties of the compartments or unit dose article,

depending on the application thereof and the required needs. For example, it may be preferred that a mixture of polymers is present in the film, whereby one polymer material has a higher water-solubility than another polymer material, and/or one polymer material has a higher mechanical strength than another polymer material. Using copolymers and mixtures of polymers can have other benefits, including improved long-term resiliency of the water-soluble or dispersible film to the detergent ingredients. For instance, US 6,787,512 discloses polyvinyl alcohol copolymer films comprising a hydrolyzed copolymer of vinyl acetate and a second sulfonic acid monomer, for improved resiliency against detergent ingredients. An example of such a film is sold by Monosol of Merrillville, Indiana, US, under the brand name: M8900. It may be preferred that a mixture of polymers is used, having different weight average molecular weights, for example a mixture of polyvinyl alcohol or a copolymer thereof, of a weight average molecular weight of from 10,000 to 40,000, and of another polyvinyl alcohol or copolymer, with a weight average molecular weight of from 100,000 to 300,000.

Also useful are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blends such as polylactide and polyvinyl alcohol, achieved by the mixing of polylactide and polyvinyl alcohol, typically comprising 1 to 35 % by weight polylactide and from 65 % to 99 % by weight of polyvinyl alcohol. The polymer present in the film may be from 60% to 98% hydrolysed, more preferably from 80% to 90%, to improve the dissolution/dispersion of the film material.

The water-soluble or dispersible film herein may comprise additive ingredients other than the polymer or copolymer material. For example, it may be beneficial to add: plasticisers such as glycerol, ethylene glycol, diethyleneglycol, propylene glycol, sorbitol and mixtures thereof; additional water; and/or disintegrating aids.

Other suitable examples of commercially available water-soluble films include polyvinyl alcohol and partially hydrolysed polyvinyl acetate, alginates, cellulose ethers such as carboxymethylcellulose and methylcellulose, polyethylene oxide, polyacrylates and combinations of these. Most preferred are films with similar properties to the polyvinyl alcohol comprising film known under the trade reference M8630, sold by Monosol of Merrillville, Indiana, US.

Process of Making:

The present invention also provides for a preferred process of making a non-aqueous composition of the present invention, comprising the steps of (i) providing a cationic polymer dispersion by combining the cationic polymer with the polypropylene glycol and (ii) combining the cationic polymer dispersion with a non-aqueous liquid feed. Preferably, the cationic polymer dispersion comprises from 1 % to 35 %, more preferably from 10 % to 25 % by weight of the cationic polymer. Since the cationic polymer is in particulate form, the viscosity of the cationic polymer dispersion remains low and it can be easily incorporated into the non-aqueous liquid feed

by typical mixing methods. The non-aqueous feed may comprise some or all of the remaining ingredients, including anionic and/or nonionic surfactants.

The process may include a step of forming an external structurant premix, and combining the external structurant premix with the cationic polymer dispersion, or the non-aqueous feed, or the combined cationic polymer dispersion/non-aqueous feed. Preferably, the external structurant premix comprises a structurant selected from hydrogenated castor oil, hydrophobically modified ethoxylated urethanes, hydrophobically modified alkali swellable emulsions, and mixture thereof. More preferably, the external structurant premix comprises a structurant selected from hydrophobically modified ethoxylated urethanes, hydrophobically modified alkali swellable emulsions, and mixture thereof.

The non-aqueous liquid composition can be comprised in a unit dose article. Such unit dose article can be prepared according to methods known in the art. For instance, the water-soluble or dispersible film is cut to an appropriate size, and then folded to form the necessary number and size of compartments. The edges are then sealed using any suitable technology, for example heat sealing, wet sealing or pressure sealing. Preferably, a sealing source is brought into contact with said film, and heat or pressure is applied to seal the film material.

The water soluble or dispersible film is typically introduced to a mould and a vacuum applied so that said film is flush with the inner surface of the mould, thus forming an indent or niche in said film material. This is referred to as vacuum-forming. Another suitable method is thermo-forming. Thermo-forming typically involves the step of forming a water-soluble or dispersible film in a mould under application of heat, which allows said film to deform and take on the shape of the mould.

Typically more than one piece of water-soluble or dispersible film material is used for making the unit dose article. For example, a first piece of film material can be vacuum pulled into the mould so that said first piece of film material is flush with the inner walls of the mould. A second piece of film material can then be positioned such that it completely overlaps with the first piece of film material. The first piece of film material and second piece of film material are sealed together. The first and second pieces of water-soluble or dispersible film can be made of the same material or can be different materials.

In a process for preparing a multi-compartment unit dose article, a piece of water-soluble or dispersible film material is folded at least twice, or at least three pieces of film material are used, or at least two pieces of film material are used wherein at least one piece of film material is folded at least once. The third piece of film material, or a folded piece of film material, creates a barrier layer that, when the film materials are sealed together, divides the internal volume of the unit dose article into two or more compartments.

A multi-compartment unit dose article may also be prepared by fitting a first piece of film material into a mould. A composition, or component thereof, can then be poured into the mould. A pre-formed compartment can then be placed over the mould containing the composition, or component thereof. The pre-formed compartment also preferably contains a composition, or component thereof. The pre-formed compartment and said first piece of water-soluble or dispersible film material are sealed together to form the multi-compartment unit dose article.

TEST METHODS:

1) Method of measuring particle size:

The Occhio Flow Cell FC200-S (Angleur, Belgium) is used to measure the particle size distribution. The sample containing the particles to be analysed is diluted to 1 % by weight, using DPG (dipropylene glycol), to ensure single particle detection. 2 ml of the diluted sample is analysed according to the instructions provided with the device.

2) Method of measuring the solubility of water-soluble or dispersible films:

5.0 grams \pm 0.1 gram of the water-soluble or dispersible film is added in a pre-weighed 400 ml beaker and 245ml \pm 1ml of distilled water is added. This is stirred vigorously on a magnetic stirrer set at 600 rpm, for 30 minutes. Then, the mixture is filtered through a sintered-glass filter with a pore size of maximum 20 microns. The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersibility can be calculated.

3) Method of measuring the dissolution time of water-soluble or dispersible films:

The film is cut and mounted into a folding frame slide mount for 24 mm by 36 mm diapositive film, without glass (part number 94.000.07, supplied by Else, The Netherlands, however plastic folding frames from other suppliers may be used). A standard 600 ml glass beaker is filled with 500 ml of city water at 10°C and agitated using a magnetic stirring rod such that the bottom of the vortex is at the height of the 400 ml graduation mark on the beaker.

The slide mount is clipped to a vertical bar and suspended into the water, with the 36 mm side horizontal, along the diameter of the beaker, such that the edge of the slide mount is 5 mm from the beaker side, and the top of the slide mount is at the height of the 400 ml graduation mark. The stop watch is started immediately the slide mount is placed in the water, and stopped when the film fully dissolves. This time is recorded as the "film dissolution time".

EXAMPLES

Cationically modified hydroxyethyl cellulose (LK400, ex-DOW), having a weight average molecular weight of 400,000 g/mol and 0.5% nitrogen substitution, was dispersed in the following dispersants: PPG400, PEG200 (comparative), 1,2-propanediol (comparative), and glycerol (comparative), to form a 4wt% dispersion of the cationically modified hydroxyethyl cellulose. The

dispersions were left at room temperature for 1 week. In order to measure the difference in swelling, the height of the sediment, consisting of the swollen cationically modified hydroxyethyl cellulose, was measured.

The cationically modified hydroxyethyl cellulose dispersed in PEG200 swelled to a volume of 240% more than the volume of the cationically modified hydroxyethyl cellulose dispersed in PPG400. The cationically modified hydroxyethyl cellulose dispersed in 1,2-propanediol swelled to a volume of 420% more than the volume of the cationically modified hydroxyethyl cellulose dispersed in PPG400. The cationically modified hydroxyethyl cellulose dispersed in glycerol had fully dissolved after 1 week.

Cationically modified hydroxyethyl cellulose (LR400, ex-DOW), having a weight average molecular weight of 400,000 g/mol and 1% nitrogen substitution, was dispersed in the following dispersants: PPG400, PEG200 (comparative), 1,2-propanediol (comparative), and glycerol (comparative), to form a 4wt% dispersion of the cationically modified hydroxyethyl cellulose. The dispersions were left at room temperature for 1 week. In order to measure the difference in swelling, the height of the sediment, consisting of the swollen cationically modified hydroxyethyl cellulose, was measured.

The cationically modified hydroxyethyl cellulose dispersed in PEG200 swelled to a volume of 266% more than the volume of the cationically modified hydroxyethyl cellulose dispersed in PPG400. The cationically modified hydroxyethyl cellulose dispersed in 1,2-propanediol, and cationically modified hydroxyethyl cellulose dispersed in glycerol had both fully dissolved after 1 week.

Examples 1 to 7 are compositions comprising a cationic polymer in particulate form, in a non-aqueous composition comprising polypropylene glycol:

	Ex 1	Ex 2	Ex 3
Ingredient	WT %	WT %	WT %
Polymer LK400 ¹	25	25	25
Polyethyleneglycol 200 ²	12	-	-
Polypropyleneglycol 400 ²	60	68.1	72
Water	-	2.5	-
Acusol TM 880 ³	3	3	3
Acusol OP301 ⁴	-	1.4	-

	Ex 4	Ex 5	Ex 6	Ex 7
Ingredient	WT %	WT %	WT %	WT %
Linear alkyl benzene sulfonic acid	17.2	17.2	17.5	17.2
C12-14 Alkyl 3-ethoxylated sulphate acid	8.1	8.1	8.2	8.1
C12-14 alkyl 7-ethoxylate	12.0	12.0	12.1	12.0
Citric acid	0.6	0.6	0.6	0.6
Palm Kernel Fatty Acid	5.6	5.6	5.7	5.6
Cleaning polymer	4.9	4.9	5.0	4.9
Chelant	1.9	1.9	2.0	1.9
Polymer LK400 ¹	3.7	3.7	3.7	3.7
Polypropyleneglycol 400 ²	8.8	10.6	8.8	8.8
Polyethyleneglycol 200 ²	1.8	-	1.8	1.8
Acusol TM 880 ³	0.2	0.2	0.2	0.2
Glycerol	4.6	2.6	-	4.6
1,2 Propanediol	12.1	14.1	16.3	6.1
Dipropyleneglycol	-	-	-	4.5
	Ex 4	Ex 5	Ex 6	Ex 7
Ingredient	WT %	WT %	WT %	WT %
Acusol OP301 ⁴	0.3	0.3	-	0.3
MEA	pH between 7 & 8			
Water	9.1	6.0	8.7	10.5
Hydrogenated castor oil (HCO) ⁵	0.2	0.2	0.2	0.2
Others (minors+ laundry adjuncts)	up to 100%			

¹ Supplied by Dow Chemicals, Louisiana, United States

² Dow Benelux, Herbert H Dowweg Terneuzen, Netherlands

³ The Dow Chemical Company, Midland, Michigan, United States

5 ⁴ 40 wt% dispersion of a styrene/acrylate copolymer, having an average particle size of 0.17 microns

⁵ Introduced via an external structurant system premix

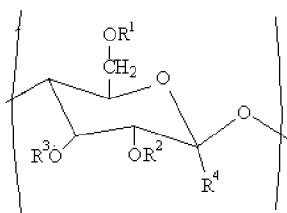
10 The non-aqueous liquid compositions of examples 1 to 7 can also be encapsulated in a water-soluble film (such as M8630, supplied by Monosol), to form stable liquid-comprising unit dose articles of the present invention.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm”.

CLAIMS

What is claimed is:

1. A non-aqueous liquid composition comprising:
 - a) a cationic polymer in particulate form; and
 - b) polypropylene glycol.
2. The non-aqueous liquid composition according any preceding claim, wherein the cationic polymer in particulate form has an volume based D90 diameter of less than 300 microns, preferably less than 200 microns, more preferably less than 150 microns.
3. The non-aqueous liquid composition according to any preceding claim, wherein the cationic polymer is a cationic polysaccharide.
4. The non-aqueous liquid composition according to claim 3, wherein the cationic polysaccharide is a cationic cellulose having the structure:



Structural Formula I

m

wherein:

m is an integer from 20 to 10,000

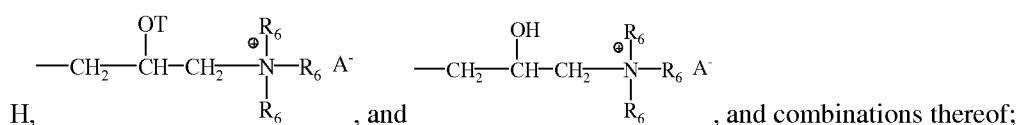
each R⁴ is H, and R¹, R², R³ are each independently selected from the group consisting of: H; C₁-C₃₂ alkyl; C₁-C₃₂ substituted alkyl, C₅-C₃₂ or C₆-C₃₂ aryl, C₅-C₃₂ or C₆-C₃₂ substituted aryl or C₆-C₃₂

alkylaryl, or C₆-C₃₂ substituted alkylaryl, and $\left(\text{CH}_2 \overset{\text{R}^5}{\underset{|}{\text{CH}}} - \text{O} \right)_n \text{Rx}$;

wherein:

n is an integer selected from 0 to 10 and

Rx is selected from the group consisting of:

A⁻ is a suitable anion;

each R_5 is independently selected from the group consisting of: H; C_1 - C_{32} alkyl; C_1 - C_{32} substituted alkyl, C_5 - C_{32} or C_6 - C_{32} aryl, C_5 - C_{32} or C_6 - C_{32} substituted aryl, C_6 - C_{32} alkylaryl, C_6 - C_{32} substituted alkylaryl, and OH;

each R_6 is independently selected from the group consisting of: H, C_1 - C_{32} alkyl, C_1 - C_{32} substituted alkyl, C_5 - C_{32} or C_6 - C_{32} aryl, C_5 - C_{32} or C_6 - C_{32} substituted aryl, C_6 - C_{32} alkylaryl, and C_6 - C_{32} substituted alkylaryl;

each T is independently selected from the group: H, $\left(\text{CH}_2 - \overset{\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{O} \right)_v - R_5$,

$\left(\text{CH} - \overset{\text{CH}_2\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{O} \right)_v - R_5$, and $-\text{CH}_2 - \overset{\text{OH}}{\underset{|}{\text{CH}}} - \text{CH}_2 - R_5$; $-\text{CH} - \overset{\text{CH}_2\text{OH}}{\underset{|}{\text{CH}}} - \text{CH}_2 - R_5$;

each v in said polysaccharide is an integer from 1 to 10; the sum of all v indices in each R_x in said polysaccharide is an integer from 1 to 30; and in the last

$-\text{CH}_2 - \overset{\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{O} - R_5$, $-\text{CH} - \overset{\text{CH}_2\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{O} - R_5$; $-\text{CH}_2 - \overset{\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - R_5$ or $-\text{CH} - \overset{\text{CH}_2\text{OT}}{\underset{|}{\text{CH}}} - \text{CH}_2 - R_5$ group in a chain, T is always an H.

5. The non-aqueous liquid composition according to any preceding claim, comprising from 0.01 % to 30 %, preferably from 0.05 % to 25 %, more preferably from 0.1 % to 10 % by weight of the cationic polymer in particulate form.
6. The non-aqueous liquid composition according to any preceding claim, comprising from 0.05 % to 98 %, preferably from 0.5 % to 75 %, more preferably from 3 % to 68 % by weight of polypropylene glycol.
7. The non-aqueous liquid composition according to any preceding claim, wherein the polypropylene glycol has a molecular weight of from 208 g/mol to 4000 g/mol.
8. The non-aqueous liquid composition according to any preceding claim, wherein the composition further comprises from 0.1 % to 30 %, preferably from 0.5 % to 15 % of spacer particles.
9. The non-aqueous liquid composition according to claim 9, wherein the spacer particles have an volume based D90 diameter of less than 5 microns, preferably from 0.1 microns to 1 micron.

10. The non-aqueous liquid composition according to any preceding claim, wherein the composition further comprises cations, preferably selected from: alkyltrimethylammonium salts, such as C12 alkyltrimethylammonium chloride, or their hydroxyalkyl substituted analogues; and/or polyvalent anions, preferably selected from: Citric Acid; Diethylene triamine pentaacetic acid (DTPA); 1-hydroxyethane 1,1-diphosphonic acid (HEDP); Maleic acid; Polyacrylates; Polyacrylic/maleic acid copolymers; succinic acid, and mixtures thereof.
11. The non-aqueous liquid composition according to any preceding claim, wherein the composition further comprises from 0.01% to 10%, preferably from 0.1% to 4% by weight of an external structuring system.
12. The non-aqueous liquid composition according to any preceding claim, wherein the composition is enclosed in a water-soluble or dispersible film comprising: polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), or mixtures thereof.
13. A process for preparing the non-aqueous liquid composition of claim 1, characterized in that the process comprises the steps of:
 - a. providing a cationic polymer dispersion by combining the cationic polymer with the polypropylene glycol; and
 - b. combining the cationic polymer dispersion with a non-aqueous liquid feed.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/061992

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/22 C11D3/37 C11D17/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 093 769 A (BURDICK CHARLES LEE [US] ET AL) 25 July 2000 (2000-07-25)	1-11
Y	claims	12,13
X	WO 2013/095996 A1 (ROHM & HAAS [US]) 27 June 2013 (2013-06-27)	1-12
Y	claims; examples 1-2	12,13
Y	WO 2011/163371 A1 (PROCTER & GAMBLE [US]) 29 December 2011 (2011-12-29) cited in the application page 10; claims; examples	12,13
A	US 2002/193256 A1 (HARRIS WILLIAM FRANKLIN [US] HARRIS JR WILLIAM FRANKLIN [US]) 19 December 2002 (2002-12-19) claims	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 February 2015

Date of mailing of the international search report

18/02/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Pfannenstein, Heide

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/061992

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6093769	A	25-07-2000	AU 1532699 A 07-06-1999
		BG 104535 A 31-01-2001	
		BR 9814664 A 03-10-2000	
		CA 2310628 A1 27-05-1999	
		CN 1285733 A 28-02-2001	
		DE 69830741 D1 04-08-2005	
		DE 69830741 T2 01-06-2006	
		EP 1030644 A1 30-08-2000	
		ES 2244100 T3 01-12-2005	
		US 6093769 A 25-07-2000	
		WO 9925313 A1 27-05-1999	

WO 2013095996	A1	27-06-2013	AR 089418 A1 20-08-2014
		AU 2012355646 A1 03-07-2014	
		CN 104053706 A 17-09-2014	
		EP 2768887 A1 27-08-2014	
		TW 201333110 A 16-08-2013	
		US 2014350123 A1 27-11-2014	
		WO 2013095996 A1 27-06-2013	

WO 2011163371	A1	29-12-2011	AR 081982 A1 31-10-2012
		CA 2800002 A1 29-12-2011	
		CN 102959069 A 06-03-2013	
		EP 2399978 A1 28-12-2011	
		ES 2428231 T3 06-11-2013	
		JP 2013534981 A 09-09-2013	
		RU 2012148751 A 27-07-2014	
		US 2011319314 A1 29-12-2011	
		WO 2011163371 A1 29-12-2011	

US 2002193256	A1	19-12-2002	CA 2453293 A1 23-01-2003
		EP 1406712 A2 14-04-2004	
		US 2002193256 A1 19-12-2002	
		US 2003220203 A1 27-11-2003	
		WO 03006135 A2 23-01-2003	
